



Using the $^{87}\text{Sr}/^{86}\text{Sr}$ of modern and paleoseep carbonates from northern Cascadia to link modern fluid flow to the past

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ABSTRACT

Most authigenic carbonates previously recovered from the Cascadia slope have $^{87}\text{Sr}/^{86}\text{Sr}$ signatures that reflect shallow precipitation in equilibrium with coeval seawater. There is also evidence for carbonate formation supported by fluids that have been modified by reactions with the incoming Juan de Fuca plate ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7071$; Teichert et al., 2005) or with terrigenous turbidites ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70975$ to 0.71279 ; Sample et al., 1993). We report on the strontium isotopic composition of carbonates and fluids from IODP Site U1329 and nearby Barkley Canyon (offshore Vancouver Island), which have strontium isotope ratios as low as 0.70539. Whereas the strontium and oxygen isotopic compositions of carbonates from paleoseeps in the uplifted Coast Range forearc indicate formation in ambient bottom seawater, several samples from the Pysht/Sooke Fm. show a ^{87}Sr -depleted signal ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70494$ and 0.70511) similar to that of the anomalous Site U1329 and Barkley Canyon carbonates.

Our data, when analyzed in the context of published elemental and isotopic composition of these carbonates (Joseph et al., 2012), point to two formation mechanisms: 1) shallow precipitation driven by the anaerobic oxidation of methane (AOM) with $\delta^{13}\text{C}$ values as low as -50% and contemporaneous $^{87}\text{Sr}/^{86}\text{Sr}$ seawater ratios, and 2) carbonate precipitation driven by fluids that have circulated through the oceanic crust, which are depleted in ^{87}Sr . Carbonates formed from the second mechanism precipitate both at depth and at sites of deep-sourced fluid seepage on the seafloor. The ^{87}Sr -depleted carbonates and pore fluids found at Barkley Canyon represent migration of a deep, exotic fluid similar to that found in high permeability conglomerate layers at 188 mbsf of Site U1329, and which may have fed paleoseeps in the Pysht/Sooke Fm. These exotic fluids likely reflect interaction with the 52–57 Ma igneous Crescent Terrane, which supplies fluids with high calcium, manganese and strontium enriched in the non-radiogenic nucleide. Tectonic compression and dehydration reactions then force these fluids updip, where they pick up the thermogenic hydrocarbons and ^{13}C -enriched dissolved inorganic carbon that are manifested in fluids and carbonates sampled at Barkley Canyon and at Site U1329. The Crescent Terrane may have sourced cold seeps in this margin since at least the late Oligocene.

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1. Introduction

The deep hydrosphere, which includes pore waters of marine sediments and fluids circulating within the underlying oceanic crust, comprises the largest continuous aquifer system on Earth (Davis and Elderfield, 2004). Characterizing the temporal and spatial characteristics of this aquifer is the topic of active research, as fluid flow plays a critical role in modulating the mechanical, chemical, and biological processes in the lithosphere (Kastner et al., 1991; Torres et al., 2004; Fisher, 2005; Screaton, 2010; Saffer and Tobin, 2011). The most

important processes that modulate fluid composition in convergent margins include: biogenic and thermogenic degradation of organic matter with subsequent hydrocarbon formation; gas hydrate formation or dissociation; microbially mediated anoxic oxidation of methane (AOM) and associated carbonate mineral precipitation; dehydration reactions of hydrous clay minerals and opal; and alteration of the oceanic crust (e.g. Han and Suess, 1989; Kastner et al., 1991; Sample, 1996; Elderfield et al., 1999; Torres et al., 2004; Screaton, 2010). Through these reactions, fluids acquire geochemical and isotopic characteristics that allow us to trace their origin and flow pathways.

Marine cold seeps, where pore fluids with exotic composition discharge at the seafloor, serve as a window into different depth levels of the deep hydrosphere and as a localized foci for the introduction of

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methane carbon to the ocean and potentially to the atmosphere (e.g. Torres et al., 2002; Riedel et al., 2006; Kim et al., 2011). Authigenic carbonates are a common feature at cold seeps (e.g. Han and Suess, 1989; Campbell et al., 2002; Greinert et al., 2002). Because these deposits remain in the geologic record, they provide valuable information to reconstruct the history of methane discharge, the processes transforming methane–carbon to carbonate, and the sources and pathways of the fluid transporting carbon. As such, authigenic carbonate analysis provides a history of evolving fluid processes in the deep hydrosphere (Sample and Reid, 1998).

Among the various geochemical tracers commonly used to fingerprint authigenic carbonates, $^{87}\text{Sr}/^{86}\text{Sr}$ is particularly valuable in tracing fluid–rock reactions, sources, and fluid mixing (e.g. Torres et al., 2004; Teichert et al., 2005; Solomon et al., 2009) because of the distinct composition of the various end-member fluids. Potential source materials responsible for the $^{87}\text{Sr}/^{86}\text{Sr}$ of interstitial waters are: continental detritus from the area bordering the Cascadia margin ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7119\text{--}0.7133$), biogenic calcite ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7068\text{--}0.7092$), and the oceanic crust ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7030$) (Veizer, 1989). The seawater $^{87}\text{Sr}/^{86}\text{Sr}$ has varied through geologic time due to varying inputs of continental detritus and hydrothermal circulation within the oceanic crust (Burke et al., 1982; Veizer, 1989). Carbonates precipitate in equilibrium with the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the fluids from which they form (Hess et al., 1986). Therefore, the strontium isotopic composition of authigenic carbonate provides a spatially resolved context for evaluating ancient fluid flow.

Previous studies have documented extensive carbonate formation at cold seeps on the Cascadia slope, where precipitation is driven by the anaerobic oxidation of methane (AOM). AOM-derived carbonates are characterized by very negative $\delta^{13}\text{C}$ values and seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Sample and Reid, 1998). Carbonates sampled along a vertical fault zone at the deformation front of the accretionary wedge show extreme ^{18}O depletion and radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.70975–0.71279), indicative of deep dewatering and flow through terrigenous turbidites (Sample et al., 1993). Here we report on the $^{87}\text{Sr}/^{86}\text{Sr}$ of authigenic carbonates and pore fluids from the Integrated Ocean Drilling Program (IODP) Site U1329 and the nearby Barkley Canyon (Fig. 1), a known thermogenic gas-rich province south of Vancouver Island (Pohlman et al., 2005; Pohlman et al., 2009; Riedel et al., 2010). We compare these results with pore water data and with paleoseep authigenic carbonates from Oligocene and Pliocene sedimentary formations of the uplifted Coast Range forearc in Washington State (Martin, 2010; Joseph et al., 2012; Nesbitt et al., 2012) to identify sources and pathways of fluid flow in the modern and ancient Cascadia margin.

2. Site descriptions

The Cascadia margin off the coast of Vancouver Island forms in response to nearly orthogonal convergence of the Juan de Fuca plate with North America, at a present rate of about 45 mm/year (Riddihough, 1984). Seaward of the deformation front, the Cascadia basin consists of pre-Pleistocene hemipelagic sediments overlain by rapidly accumulating Pleistocene deposits. Most of the incoming sediment is scraped off the oceanic crust and folded and thrust upward to form a thick accretionary prism. Depositional coarse-grained turbidite layers and tectonically driven fractures and thrust faults act as high permeability migration pathways for deep-sourced fluids (Tréhu et al., 1994; Hyndman, 1995). As fluids ascend through the sediment column, pressure drops resulting in carbonate precipitation (e.g. Sample, 1996) (Table 1).

Site U1329 was drilled within the modern accretionary prism during the IODP Expedition 311, 65 km offshore in a water depth of 946 mbsl (Riedel et al., 2006). The sediment section recovered at this site is divided into three lithostratigraphic units. Unit I (<37 mbsf) is characterized by clay and silty clay sediment locally interbedded with coarse-grained sediments. Unit II (37–135.6 mbsf) is characterized by a transition to

a diatom ooze. A layer of rounded conglomerate clasts that corresponds to an unconformity between upper Miocene and Pleistocene sediments marks the lithostratigraphic boundary between Units II and III. Unit III is characterized by clay to silty-clay detrital sediments with a few interlayered, coarse turbidite deposits. Another conglomerate layer sampled at 188 mbsf marks the base of Unit III and represents the deepest drilled section at Site U1329 (Riedel et al., 2006). This conglomerate consists of carbonate cemented sandstone/quartzite and mudstone clasts up to 4 cm in diameter (Fig. 2).

Barkley Canyon is a headless submarine canyon located about 100 km off the west coast of Vancouver Island at 850 mbsl. Previously recovered thermogenic gases and gas hydrates were used to suggest that Barkley Canyon acts as a focus for discharge of deep-sourced fluids within the Cascadia subduction zone (Pohlman et al., 2005). Authigenic carbonate samples and pore fluids from this site were collected from piston cores during a Pacific Geoscience Centre expedition in 2008 (samples BC1–BC4) and seafloor grabs and push cores collected using the remotely operated vehicle (ROV) Doc Ricketts during the MBARI Pacific Northwest Expeditions in 2009 (BC5–BC6) and 2011 (BC7–BC13) (Joseph et al., 2012).

Fossil cold seeps within the uplifted accretionary wedge sequences of the Olympic Mountains in Washington, USA were identified by the presence of fossilized chemosynthetic invertebrate communities and have been previously described by Martin (2010), Torres et al. (2010), and Nesbitt et al. (2012). Paleoseep carbonate petrology and geochemistry is reported in Joseph et al. (2012). We build on these results by analyzing the strontium isotopic composition of authigenic carbonates from the Pliocene Quinault Formation (southern Olympic Peninsula) and from the Oligocene–Miocene Sooke (southern Vancouver Island) and Pysht Formations (northern Olympic Peninsula).

The Pysht Formation is typified by 1 km thick pelagic and fine grained turbidite deposits. The Sooke Formation consists of inner neritic to supratidal sandstones and conglomerates. These two formations are part of the same submarine fan incised by the Strait of Juan de Fuca. We will refer to them jointly in this study. The Quinault Fm. is typified by 3 km of outer-shelf to estuarine storm-dominated deposits with a localized distribution of fossilized seep organisms (Campbell, 1992).

Underlying the paleoseep host formations is the Eocene Crescent Formation, which is known as the Siletz River Formation in Oregon and as the Metochosin Formation on Vancouver Island (Snively et al., 1968; Tréhu et al., 1994). The Crescent Formation is the most voluminous of all Coast Range volcanic sequences, consisting of pillowed and massive basaltic flows up to 15 km thick (Brandon et al., 1998). It may have originated as a result of the accretion of an oceanic island or seamount (e.g. Duncan, 1982; Johnston and Acton, 2003) or as an accreted oceanic plateau (Babcock et al., 1992). This 52–57 Ma igneous terrane comprises the basement unit of the Coast Range and Olympic Mountains throughout Washington and Oregon and forms the modern crystalline backstop to the northern Cascadia accretionary complex landward of Barkley Canyon and Site U1329 (Fig. 1).

3. Methods

The pore water strontium isotopic composition for Site U1329 was available from the literature (Riedel et al., 2010). The analytical techniques and the elemental and isotopic composition of carbon and oxygen for carbonate samples used in this study are presented in Joseph et al. (2012). We measured the strontium isotopic composition of authigenic carbonates and pore fluids from Barkley Canyon and of carbonates recovered from Site U1329 and from exposed paleoseep formations. The same Sr-separation technique was used for both carbonates and pore fluids.

Pore fluids from Barkley Canyon were collected from Core 23 during the PGC2008-007 expedition using pre-soaked Rhizone samplers to a maximum depth of 190 cmbsf. For $^{87}\text{Sr}/^{86}\text{Sr}$ analysis, 50 μl of pore

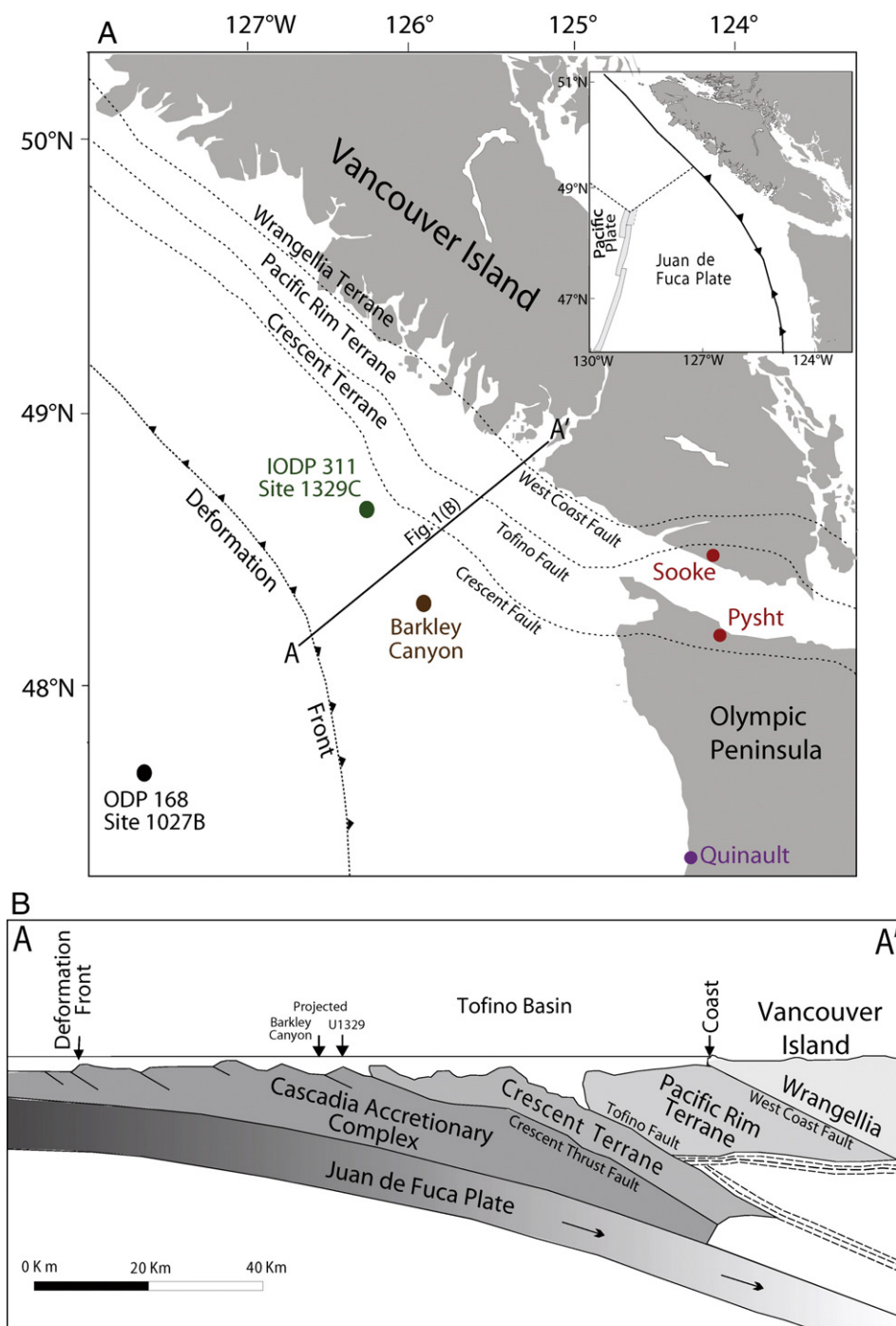


Fig. 1. Map of sample locations after Kim et al. (2011). Cross-section adapted from Hyndman et al. (1990).

fluid was dried and brought to 500 μ l with 1 N HCl. Carbonate samples were first dried at 60 $^{\circ}$ C for 24 h and then ground into powder with a mortar and pestle. 10 mg of powdered sample was placed in an acid-washed Teflon vial and acidified with 4 ml of 25% (4 N) CH_3COOH . An additional 4 ml of 25% CH_3COOH was added if the initial volume failed to dissolve the whole sample. This solution was then refluxed at 70 $^{\circ}$ C for 12 h, sonicated for 30 min, centrifuged and decanted into Teflon vials. Pore fluids were directly loaded into the separation columns after acidification.

Strontium separation was carried out using a 50 μ l Sr-specific column and resin from EICHRON. Isotopic analysis of a solution containing 300 ng Sr was performed using the Nu multi-collector inductively coupled mass spectrometer (MC-ICPMS) housed in the W.M. Keck

Collaboratory for Plasma Spectrometry in the College of Oceanic and Atmospheric Science at Oregon State University (OSU-COAS). Reagent and column blanks contained < 10 ng Sr. $^{87}\text{Sr}/^{86}\text{Sr}$ data was normalized to the NBS 987 (National Bureau of Standards) standard, with a reported $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.71024. A mean value of 0.71022 ± 0.00005 ($2\sigma_{\text{mean}}$, $n=91$) was obtained for repeated measurements. Replicate analysis of an in house standard yielded a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70817 ± 0.00005 ($2\sigma_{\text{mean}}$, $n=79$).

4. Results

The strontium isotopic composition of Barkley Canyon samples is listed in Table 2. Pore fluids from Core 23 have a modern seawater

Table 1
Site and sample locations.

Site and sample designation	Latitude (N)	Longitude (W)	Water depth
<i>Modern seafloor sites</i>			
Site U1329	48.79	126.68	953 mbsl
Barkley Canyon			850 mbsl
PGC C23	48.3107	126.0666	
DR59	48.1782	126.0652	
DR271	48.1756	126.0973	
DR273	48.3109	126.0651	
<i>Paleoseeps on land</i>			Age
<i>Pysht Formation</i>			
Pysht Tree Farm	48.2203	124.1303	Oligocene
Pysht Quarry	48.1856	124.0811	Oligocene
Sooke Formation	48.4944	124.3261	Oligocene
Quinault Formation	47.3844	124.3236	Pliocene

isotopic signal ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70917$) from the seafloor to 171 mbsf, but below this depth deviate from the seawater value to a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70878 measured at 196 mbsf (Fig. 3). Of the 13 authigenic carbonates analyzed from Barkley Canyon, nine carry a $^{87}\text{Sr}/^{86}\text{Sr}$ signal consistent with formation in equilibrium with modern seawater. The remaining four samples (BC5, BC10, BC12, and BC13) suggest the contribution of fluids that have been modified by reactions with igneous material (Fig. 3). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of samples BC5 and BC12 (0.70652 and 0.70574) are the lowest reported in shallow sediments of the Cascadia margin.

Non-radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were also measured in carbonates and pore waters sampled from a conglomerate layer at the base of Site U1329 (Fig. 4). The high permeability conglomerate layer is centered at 188 mbsf and may represent a debris flow (Riedel et al., 2006). Carbonates U1329-10 and U1329-11 were sampled from within this conglomerate and display significant ^{87}Sr depletion, with $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.70539 and 0.70542, respectively (Fig. 4). Pore fluid data are consistent with active flow through this conglomerate (Kim et al., 2011). In the upper 60.5 mbsf, pore fluids from Site U1329 display a contemporaneous seawater signal when adjusted for variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater through geologic time (Burke et al., 1982; Veizer, 1989). Below this depth there is a monotonic decrease in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, with the lowest value measured on a sample collected immediately above the conglomerate layer.

Consistent with observations in the modern marine settings, the paleoseep carbonate samples also carry Sr-isotope signals that range from age-adjusted contemporaneous seawater values to values similar to but more depleted than the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios found at depth at Site U1329. Carbonates from the Pliocene Quinault Formation all indicate formation in equilibrium with Pliocene seawater, with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that range from 0.70874 to 0.70891 (Table 2) (Veizer, 1989). Similarly, the Pysht/Sooke Fm. samples PS2 and PS7 also indicate formation in equilibrium with contemporaneous (Late Oligocene) seawater, with a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of ~0.7080 (Veizer, 1989). In contrast, samples PS1 and PS3 are significantly depleted relative to the Oligocene seawater value and display $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70511 and 0.70494, respectively (Table 2). These anomalous carbonates were identified as fracture fill precipitants based on observed cross-cutting relationships between the carbonate veins and the host formation (Joseph et al., 2012; Nesbitt et al., 2012) and are likely to reflect secondary precipitation spurred by flow of deep-sourced fluids that had been modified by reaction with igneous crust.

5. Discussion

Carbonates formed from fluids whose composition has been modified by fluid–rock interactions at depth record the geochemical and isotopic characteristics of that interaction. These fingerprints are incorporated into authigenic minerals, which then serve as a valuable

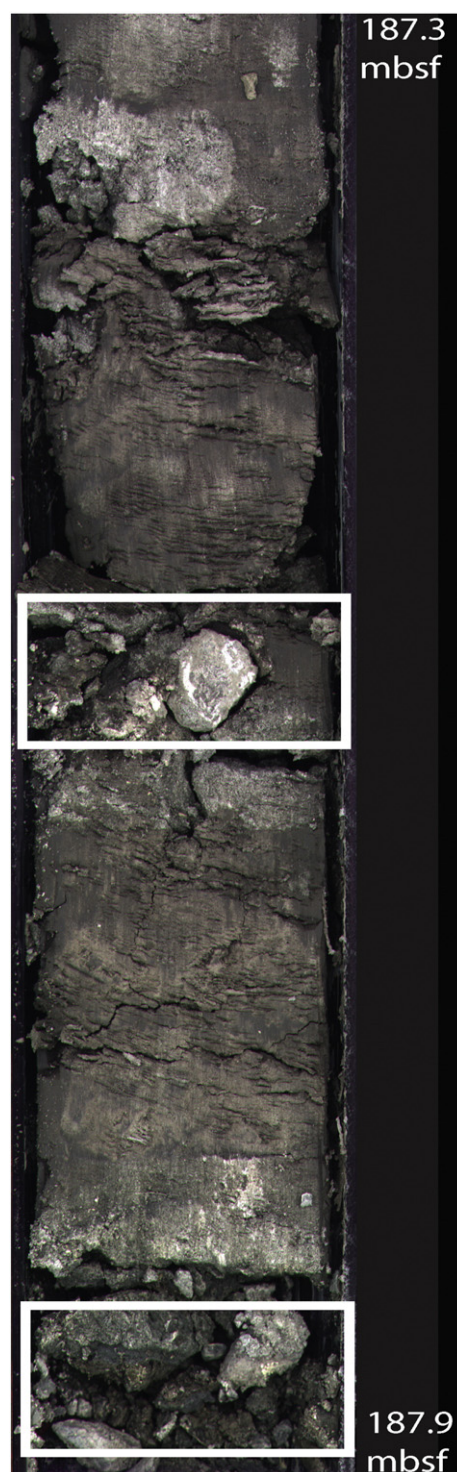


Fig. 2. Core section from the base of Site U1329 showing the 188 mbsf conglomerate layer. White boxes indicate sample locations for ^{87}Sr -depleted samples U1329-10 and U1329-11. Scale bar in cm.

proxy for the nature and conditions that were present during periods of paleo fluid flow. Joseph et al. (2012) showed that carbonates formed from deep sourced, reducing, diagenetic fluids in the Cascadia margin tend towards ^{13}C -enrichment, ^{18}O -depletion, and elevated Mn/Ca ratios. These variables correlate with $^{87}\text{Sr}/^{86}\text{Sr}$ data such that carbonates with deep-sourced attributes are also depleted in ^{87}Sr (Fig. 5).

Barkley Canyon taps a thermogenic hydrocarbon source (Pohlman et al., 2005) that is immediately juxtaposed with a microbial methane

Table 2

Carbonate chemistry and isotopes.

Barkley Canyon carbonate chemistry was taken from Joseph et al. (2012). Paleoseep chemistry was from Torres et al. (2010).

Cruise sample name	Lab sample name	Depth (mbsf)	Mg/Ca mmol/mol	Mn/Ca	Sr/Ca	Ba/Ca	$\delta^{13}\text{C}$ ‰ PDB	$\delta^{18}\text{O}$	$^{87}\text{Sr}/^{86}\text{Sr}$
<i>IODP 311 Site U1329C</i>									
04H-03W 92-94	U1329-1	31.0	804.3	5.9	1.1	0.9	−21.3	7.1	0.70917
04H-03W 140-142	U1329-2	31.5	790.2	3.2	1.2	0.9	−22.9	7.3	0.70917
08H-2W 63-65	U1329-3	59.7	208.3	1.0	1.8	0.6	−29.3	5.1	0.70916
08H-2W 71-73	U1329-4	59.8	173.4	0.6	2.1	0.8	−30.2	4.8	0.70921
17H-01 W	U1329-5	135.6	172.9	1.2	1.7	1.2	−12.0	4.9	0.70897
18X-02W 8-10	U1329-6	141.8	661.4	4.6	1.5	1.9	5.2	6.5	0.70862
18X-5W	U1329-7	146.6	139.7	0.9	2.1	1.3	−20.3	4.0	0.70898
20X-03W 35-37	U1329-8	163.0	169.9	0.5	1.9	0.8	−20.9	4.3	0.70892
21X-03W 63-65	U1329-9	172.9	110.4	5.0	2.1	1.9	−13.0	3.6	0.70819
22X-CCW 44-46 160.3	U1329-10	187.5	71.2	17.9	0.7	0.2	5.4	−10.8	0.70542
22X-CCW 70-72	U1329-11	187.8	48.4	16.4	0.7	0.2	5.8	−10.1	0.70539
<i>Barkley Canyon</i>									
PGC C23 AB 110–120cm	BC1	1.16	229.7	0.70	1.59	0.16	−24.9	4.7	0.70918
PGC C23 AB 150 cm	BC2	0.76	221.1	0.47	1.56	0.23	−19.6	4.9	0.70913
PGC C23 AB 170 cm	BC3	0.56	207.5	0.59	1.80	0.40	−24.0	4.3	0.70918
PGC C23 AB 200 cm	BC4	0.26	233.8	0.80	1.73	0.16	−21.3	4.8	0.70915
DR59 PsC 46	BC5	0.08	107.7	8.50	2.40	0.15	−4.6	−8.6	0.70652
DR59 PsC 44	BC6	0.22	54.0	0.75	12.14	0.22	−20.5	3.9	0.70916
DR271 – R1	BC7	Seafloor	50.0	0.45	10.66	0.05	−47.6	4.1	0.70917
DR271 – R2	BC8	Seafloor	9.2	0.09	10.41	0.04	−45.4	4.1	0.70915
DR271 – R3	BC9	Seafloor	8.4	0.05	9.61	0.03	−43.4	4.1	0.70916
DR271 – PC41 4 cm	BC10	0.04	255.6	0.68	1.58	0.10	−50.9	5.3	0.70865
DR273 – PC41 10 cm	BC11	0.10	5.8	0.03	12.84	0.25	−22.2	3.9	0.70916
DR273 – PC41 5 cm	BC12	0.05	317.7	13.35	1.90	0.49	−4.9	−9.3	0.70574
DR273 – PC66 18 cm	BC13	0.18	187.8	0.51	1.65	0.10	−11.4	4.9	0.70897
<i>Pysht/Sooke Formation</i>									
	PS1		64.4	10.4	1.55	0.28	7.4	−5.6	0.70511
	PS2		415.0	60.7	1.50	0.98	7.0	1.5	0.70794
	PS3		18.3	23.4	0.71	8.44	5.9	−11.6	0.70494
	PS7		32.0	5.30	0.98	0.70	−29.6	0.4	0.70799
<i>Quinault Formation</i>									
	Q4		68.7	2.47	1.83	0.17	−15.4	1.8	0.70882
	Q5		76.8	4.04	1.76	0.19	−21.7	1.0	0.70875
	Q6		69.9	3.02	1.55	0.15	−14.0	1.6	0.70874
	Q9		84.4	4.25	1.95	0.20	−27.3	1.4	0.70891

source (Joseph et al., 2012). Seeps in this canyon display large spatial heterogeneity, similar to that reported on the Heceta shelf and slope on the central Cascadia margin (Torres et al., 2009) and as far south as the Eel River Basin seeps (Kvenvolden and Field, 1981; Brooks et al., 1991). All these reports highlight the complex hydrology of the margin, where adjacent microbial and thermogenic hydrocarbon sources feed methane to the bottom water (e.g. Heeschen et al., 2005; Torres et al., 2009).

Because thermogenic hydrocarbons form at depth, deep-seated migration pathways are required for them to manifest in the fluids discharging from the seafloor and in gas hydrate deposits (Pohlman et al., 2005). The thermogenic nature of the carbon source is preserved as relatively ^{13}C -enriched carbonates that form when the discharging methane is oxidized by microbial activity at the seafloor (Joseph et al., 2012). The fact that most of the Barkley Canyon carbonates have a seawater $^{87}\text{Sr}/^{86}\text{Sr}$ composition and show negative $\delta^{13}\text{C}$ values (as low as -50%) indicates that these carbonates formed from oxidation of microbially generated methane (Group I in Fig. 5), rather than from a deep thermogenic carbon source such as that sampled in nearby seeps by Pohlman et al. (2005). The two carbonate samples that display more positive $\delta^{13}\text{C}$ values (BC5 and BC12) also show less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values relative to the other 11 samples collected at this site (Group II, Fig. 5). These samples are depleted in ^{18}O ($\delta^{18}\text{O} = -8.6\%$ and -9.3% , respectively) and likely reflect precipitation from a deep-seated fluid source that has interacted with the oceanic crust and has experienced temperatures high enough to drive thermogenic hydrocarbon formation. Upward fluid migration of these warm fluids along high permeability horizons is then revealed by the

thermogenic gases sampled at seep sites by Pohlman et al. (2005) and carbonates with distinct isotopic ratios (Group II), as illustrated by samples BC5 and BC12 in Fig. 5A and B.

With the exception of the two deepest samples, U1329-10 and U1329-11, carbonates from Site U1329 fall within the same $\delta^{13}\text{C}$ range as those from Group I in Barkley Canyon (Table 2; Fig. 5). Whereas this heavy signal is usually taken to indicate a thermogenic gas source, Pohlman et al. (2009) attributed the heavy $\delta^{13}\text{C}_{\text{CH}_4}$ at Site U1329 to a kinetic isotope effect. The low sedimentation rates and prolonged degradation of organic matter in the sulfate reduction zone of the sediment column progressively deplete organic matter in ^{12}C and create a microbial gas enriched in ^{13}C relative to a typical microbial methane source ($\delta^{13}\text{C} < -50\%$ PDB). This interpretation is adopted to explain the carbon source for carbonates U1329-1 to U1329-9. However, the heavy $\delta^{13}\text{C}$ of U1329-10 and U1329-11 (5.89‰ and 5.67‰ PDB, respectively) reveal formation from a deep, residual, isotopically heavy dissolved inorganic carbon pool, which at this site has a $\delta^{13}\text{C} \sim 30\%$ (Torres and Kastner, 2008). Consistent with the carbon isotopic evidence, these carbonates are also highly depleted in ^{87}Sr , which indicates formation driven by flow of ^{87}Sr -depleted fluids through a conglomerate layer.

The dissolved carbon that supports formation of Group II carbonates BC5 and BC12 (sampled near the seafloor at Barkley Canyon) and U1329-10 and U1329-11 (sampled at 188 mbsf at Site U1329) combined with the strontium isotopic composition of these samples is consistent with a deep fluid source that has interacted with the oceanic crust. These samples are also depleted in ^{18}O and have high Mn/Ca ratios (Fig. 5B, C; Table 2). Fluid–rock interaction in basalt source reservoirs at elevated temperatures results in Ca and Mn enrichment

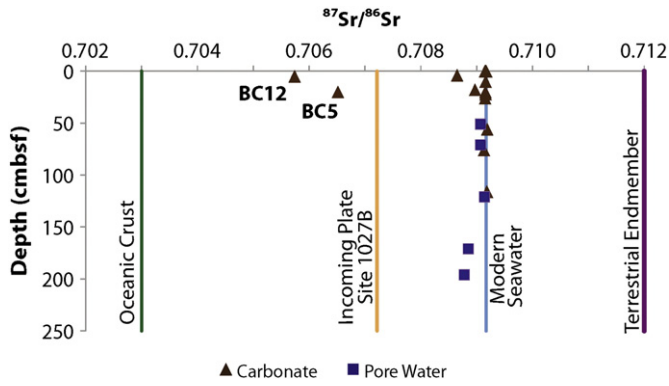


Fig. 3. $^{87}\text{Sr}/^{86}\text{Sr}$ from pore fluids (blue squares) and carbonates (brown triangles) at Barkley Canyon. Pore fluids indicate a contribution from an igneous source below 100 cmbsf. Carbonate samples BC5 and BC12 are more depleted than the most depleted values reported in northern Cascadia from the incoming plate, indicative of a different, more evolved fluid source. We interpret this signal to indicate water–rock interaction with oceanic crust of the Crescent Formation. Terrestrial end-member (~0.712) and oceanic crust values (~0.703) are adopted from Veizer (1989). Incoming plate value at Site 1027B is from Mottl et al. (1998).

(Seyfried, 1977; Wheat and Mottl, 2000; Claesson et al., 2004). The high calcium and alkalinity (20 mM) concentration of the deep fluids sampled at the conglomerate layers of Site U1329 (Riedel et al., 2006) likely triggered carbonate precipitation within this horizons. Thus, the elevated Mn/Ca ratios in samples depleted in ^{87}Sr of Group II carbonates are highly consistent with migration of fluids that have interacted with the oceanic crust. Carbonate precipitation at elevated temperatures is known to result in a depletion of ^{18}O relative to the attendant formation fluids. Because we do not know the ^{18}O of the fluids from which carbonate precipitation occurred, we are unable to estimate their formation temperature. Nonetheless it is apparent that all deep-sourced Group II carbonates are depleted in ^{18}O .

The ^{87}Sr depletion and high Mn/Ca ratios of fracture fill carbonates PS1 and PS3 from the Pysht/Sooke Fm. are similar to the Group II carbonates sampled from Site U1329 and Barkley Canyon. Sample PS3 has the most depleted $\delta^{18}\text{O}$ value of any carbonate analyzed and shows a petrographic character similar to ^{87}Sr -depleted sample BC5 (Joseph et al., 2012).

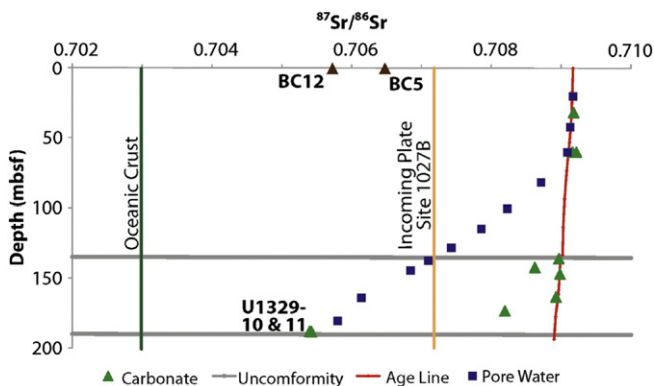


Fig. 4. $^{87}\text{Sr}/^{86}\text{Sr}$ of carbonates (green triangles) and pore fluids (blue squares) from Site U1329. Pore fluids indicate conservative mixing between seawater and an ^{87}Sr -depleted fluid sampled from an unconformity at 188 mbsf. Carbonates that fall on the age line indicate formation with the contemporaneous seawater $^{87}\text{Sr}/^{86}\text{Sr}$ value. Age line was calculated using sedimentation rates (Riedel et al., 2006) and variations in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ through time (Veizer, 1989). Further depletion of pore fluids and carbonates below the incoming plate Site 1027B value is indicative of a more evolved fluid source. Carbonates BC5 and BC12 from Barkley Canyon (brown triangles) were included for comparison.

Teichert et al. (2005) identified an eastward increase in the basaltic component of the Sr-isotopic composition of pore fluids with distance from the deformation front offshore central Cascadia. All pore fluids analyzed between the central Oregon coast and Vancouver Island have $^{87}\text{Sr}/^{86}\text{Sr}$ values that follow the mixing curve between seawater (0.70917) and the end-member value for Site 1027B (0.7071);

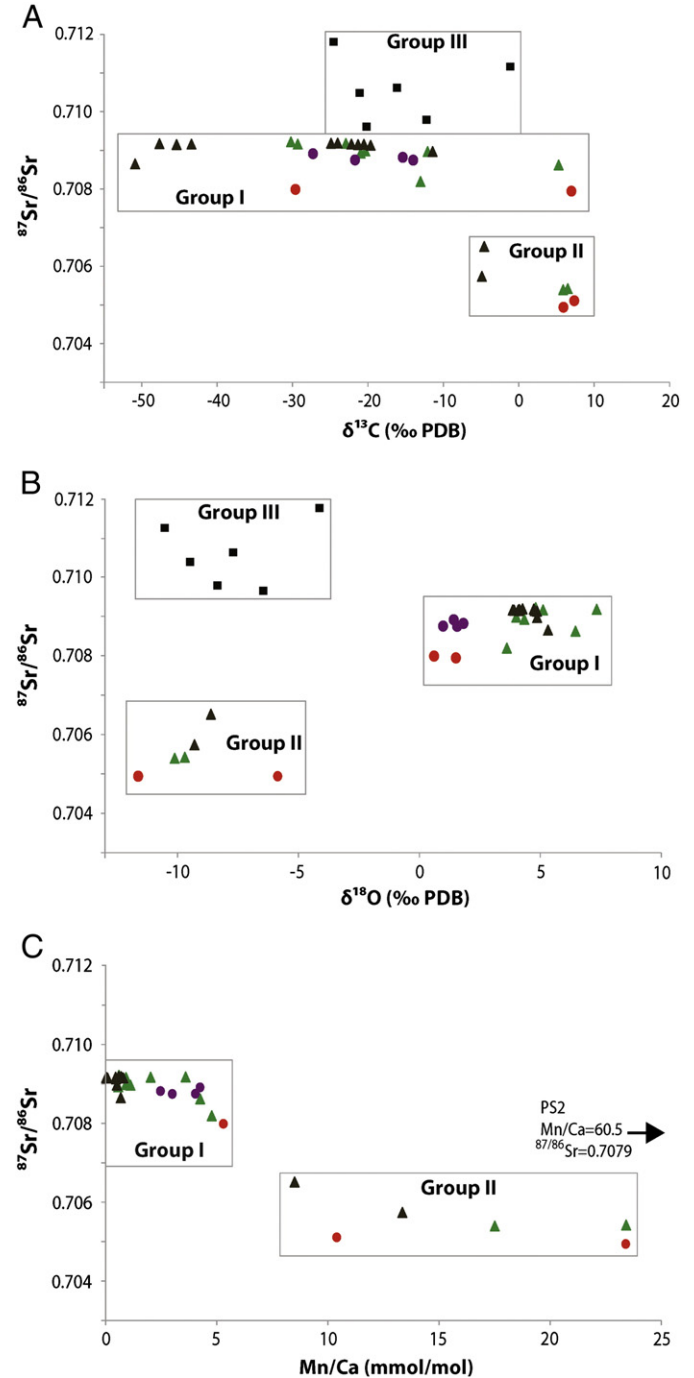


Fig. 5. Isotopic composition of all carbonates analyzed. Group I carbonates indicate formation from the anaerobic oxidation of methane in equilibrium with contemporaneous seawater. Group II carbonates indicate formation from a warm, ^{13}C - and Mn-enriched fluid that is ^{87}Sr -depleted, indicative of a deep source fluid that has interacted with igneous material. Barkley Canyon = brown triangles, U1329 = green triangles, Pysht/Sooke Fm. = red circles, and Quinault Fm. = purple circles. Group III carbonates were taken from Sample et al. (1993) to show carbonate cementation from fluids migrating within a vertical fault at the deformation front (Mn data unavailable for these samples). $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and Mn/Ca are presented in Joseph et al. (2012).

Teichert et al., 2005; Riedel et al., 2010). This end-member value corresponds to the deepest sample from Site 1027B (Mottl et al., 1998; Elderfield et al., 1999) and is consistent with data from fluids collected from venting sites on the incoming plate (Butterfield et al., 2001). In contrast, the Site U1329 pore fluids sampled between 50 mbsf and the 188 mbsf conglomerate horizon display a conservative mixing behavior between seawater and a $^{87}\text{Sr}/^{86}\text{Sr}$ -depleted fluid, with a $^{87}\text{Sr}/^{86}\text{Sr}=0.70583$. This low $^{87}\text{Sr}/^{86}\text{Sr}$ value indicates that the fluids in the conglomerate layer sampled at Site U1329 are sourced from a fluid with a different isotopic end-member composition than that of the incoming Juan de Fuca Plate (Fig. 6). The significant enhancement of a basaltic fluid component at Site U1329, which is also evident in the deep-sourced (Group II) carbonate samples from U1329 and Barkley Canyon, is indicative of a more evolved fluid source than that which has been modified by reaction with the incoming Juan de Fuca Plate crust.

One possible source for the ^{87}Sr depletion could be fluid interaction with volcanic ash layers. It is well established that ash alteration has occurred throughout the northern Cascadia margin (e.g. Riedel et al., 2006, 2010). However, none of the fluids sampled along the central or northern Cascadia margin that carry chemical or isotopic signals associated with ash alteration show the level of ^{87}Sr depletion that we see in the anomalous pore fluids and deep-sourced carbonates from Site U1329 and Barkley Canyon.

Fluids sampled on the incoming plate at Site 1027B are ~140 km away from Site U1329. It is possible that the fluids in the Juan de Fuca crust directly underneath Site U1329 are more evolved and may have a $^{87}\text{Sr}/^{86}\text{Sr}$ composition as low as the end-member fluid sampled at 188 mbsf at this site. However, it is hard to imagine a mechanism in which fluids in contact with the subducting slab migrate towards the seafloor without modifying their strontium isotopic composition, given the geometry of the slab and the thick sediment section that separates the subducting crust from the locations where our ^{87}Sr depleted fluids were sampled. In fact, carbonate samples collected along a vertical fault that sampled very deep (>2 km) fluids at the deformation front of this margin have radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig. 5, Group III; Sample et al., 1993). These ^{87}Sr -enriched samples are thought to reflect the addition of strontium from terrigenous sediments as fluids

migrate through the extensive turbidite systems that characterize the accretionary wedge.

Given the location of the sites sampled by this study (Fig. 1), we postulate that the depleted $^{87}\text{Sr}/^{86}\text{Sr}$ signal recorded by Site U1329 and Barkley Canyon carbonates reflects fluid flow through the Crescent Terrane, which is located down-dip from our study sites. The Crescent Terrane, which serves as the crystalline backstop to the incoming plate section, is currently buried underneath a sediment slope apron. In addition, this terrane outcrops at several locations on land and underlies the paleoseep host formations. The dominant $^{87}\text{Sr}/^{86}\text{Sr}$ composition of uplifted, unweathered Crescent Terrane basalts sampled on the northern Olympic Peninsula is ~0.7032, and weathered basalts here have a $^{87}\text{Sr}/^{86}\text{Sr}$ of up to 0.7045 (Pyle, 2011, pers. comm.). Migration within the permeable crust, tectonic compression and dehydration reactions can force these fluids updip. As the fluids migrate, they pick up the thermogenic hydrocarbons and ^{13}C -enriched dissolved inorganic carbon signatures, which are manifested in anomalous fluids and Group II carbonates sampled in Barkley Canyon and at Site U1329.

An active lateral advective component to the subsurface flow within the Site U1329 conglomerate is evident by the pronounced discontinuities in the geochemical profiles (Kim et al., 2011). These investigators use anomalies in europium (Eu), lithium (Li), chloride (Cl), and potassium (K) concentrations to demonstrate that pore fluids sampled from conglomerate layers at Site U1329 harbor distinct fluids with a reducing component that has been modified by high temperature alteration of igneous rocks. Chemical and isotopic composition of carbonates sampled within the conglomerate layer at 188 mbsf demonstrates formation at depth, triggered by the high calcium and alkalinity content of the migrating fluids (Riedel et al., 2006). Active venting of ^{87}Sr -depleted fluids at Barkley Canyon, which also harbor a thermogenic hydrocarbon signature, is also part of this deep-rooted aquifer system. Carbonate samples from the Oligocene paleoseeps on the Olympic Peninsula further display a contribution of a deep fluid source, similar to the one driving modern precipitation of Group II carbonates. The deep exotic fluids likely reflect interaction with the 52–57 Ma igneous Crescent Terrane, which may have sourced cold seeps in this margin since at least the late Oligocene.

The areal extent of the Crescent Terrane spans from southern Vancouver Island to central Oregon where it is known as the Siletz River Volcanics (Snaveley and Baldwin, 1948; Johnston and Acton, 2003). Paleoseeps have been identified at coastal locations throughout this areal extent (e.g. Campbell, 1992; Peckmann et al., 2003; Torres et al., 2010). The Sr-isotope analysis of authigenic carbonates found at these paleoseeps can help elucidate the spatial and temporal extent of the deep hydrosphere that is influenced by these accreted terranes.

6. Conclusions

Carbonates characterized by ^{87}Sr and ^{18}O depletion and ^{13}C and Mn/Ca enrichment were sampled at or near the seafloor at Barkley Canyon (BC5 and BC12) and in a conglomerate layer 188 mbsf at Site U1329 (U1329-10 and U1329-11). These samples have been designated as Group II carbonates. They are distinct from Group I carbonates, which formed by precipitation near the seafloor in equilibrium with a seawater strontium isotopic composition. Pore water data from Site U1329 reveals an active lateral advective component to the subsurface flow regime. Here, migrating fluids have been modified by high temperature alteration of igneous rocks and are characterized by high alkalinity, strontium, calcium, and manganese. These fluids result in precipitation of Group II carbonates along the migration pathway.

Active fluid venting at Barkley Canyon reveals a complex hydrological regime. At this site, fluids characterized by anaerobic oxidation of microbial methane that bare a seawater strontium isotopic composition are juxtaposed to sites where deep-rooted fluids characterized by ^{87}Sr and ^{18}O depletion and ^{13}C enrichment discharge at the seafloor. Thus, the shallow carbonates collected at the Barkley Canyon sites encompass

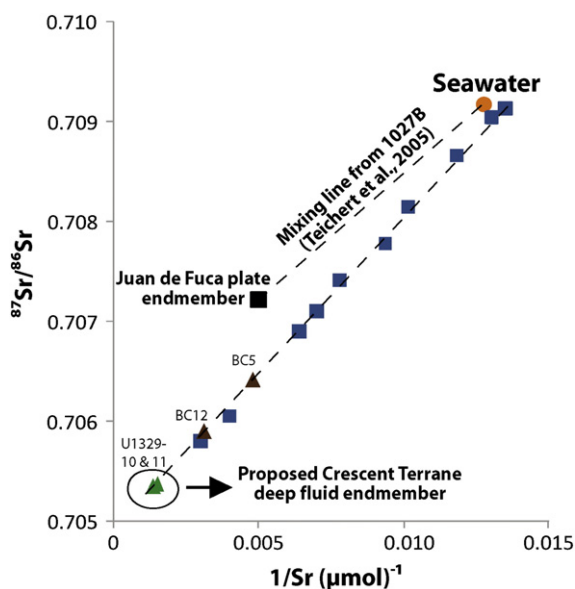


Fig. 6. End-member fluid mixing diagram showing conservative mixing between seawater and our proposed modern deep fluid end-member. Our mixing line indicates a different fluid source than that identified on the incoming Juan de Fuca plate at Site 1027B (Teichert et al., 2005).

Pore fluid data (blue squares) is from Riedel et al. (2010).

a range of compositions consistent with the variability observed in the venting fluids.

The strontium isotopic composition of pore fluids and Group II carbonates reveals a fluid end-member with a $^{87}\text{Sr}/^{86}\text{Sr}$ fingerprint that is lower than that characterizing the fluids in contact with the incoming Juan de Fuca crust. The 52–57 Ma igneous Crescent Terrane, which is located down-dip from both Barkley Canyon and Site U1329, acts as the modern crystalline backstop for the incoming plate. Given the geometry of the subducting slab and that of the emplaced Crescent Terrane relative to our study sites, we postulate that this igneous terrane acts as an extensive aquifer which supplies fluids enriched in calcium, manganese and strontium enriched in the non-radiogenic nucleide. Tectonic compression and dehydration reactions then force these fluids further up-dip, where they pick up the thermogenic hydrocarbons and ^{13}C -enriched dissolved inorganic carbon that are manifested in fluids and Group II carbonates sampled at Barkley Canyon and at Site U1329.

No other sites drilled on the Cascadia margin have the elemental and isotopic signatures that we report here. However, fracture-filled carbonates recovered from exposed paleoseeps of the Oligocene Pysht/Sooke Fm. reveal a source fluid similar in nature and origin to that supporting modern Group II carbonates in Barkley Canyon and Site U1329. We show that this tectonic and structurally driven fluid flow has sustained a long-lived hydrologic regime and attests to the complexity of the subseafloor hydrosphere.

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